CANMET

REPORT 83-9E

Canada Centre for Mineral and Energy Technology

Centre canadien de la technologie des minéraux et de l'énergie

RADIUM-226 IN CERTIFIED URANIUM REFERENCE ORES DL-1a, BL-4a, DH-1a AND BL-5

C.W. SMITH AND H.F. STEGER

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES

MAY 1983

24 pages

MICROMEDIA

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

Canada

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Canadian Government Publishing Centre
Supply and Services Canada
Ottawa, Canada, K1A 0S9

Catalogue No. M38-13/83 9E
ISBN 0-660-11465-8

Canada: $2.25
Other countries: $2.70

Price subject to change without notice

Disponible en français

RADIUM-226 IN CERTIFIED URANIUM REFERENCE ORES DL-1a, BL-4a, DH-1a AND BL-5

LE RADIUM-226 DES MINERAIS DE RÉFÉRENCE D'URANIUM DL-1a, BL-4a, DH-1a et BL-5

by/par

C.W. Smith* and/et H.F. Steger*

SYNOPSIS

Radium-226 radioactivity in uranium reference ores BL-4a and BL-5 and uranium-thorium reference ores DL-1a and DH-1a was determined in an interlaboratory program. Twelve of thirteen participants used certified radium solutions from the United States National Bureau of Standards (NBS) for calibration purposes. Recommended values of ^{226}Ra activity and associated parameters were calculated by statistical treatment of the results. In all cases, the recommended values are within 2% of activities predicted assuming secular equilibrium in the ^{238}U decay series.

The recommended values for radium activity are 1.40, 15.5, 31.5 and 857 Bq g^{-1} for DL-1a, BL-4a, DH-1a and BL-5, respectively.

La radioactivité du ^{226}Ra des minerais de référence d'uranium BL-4a et BL-5 et des minerais de référence d'uranium et de thorium DL-1a et DH-1a a été déterminée par un programme interlaboratoires. Douze des treize participants ont employé pour but de la calibration des solutions du radium certifées par le United States National Bureau of Standards (NBS). Les valeurs recommandées de la radioactivité du ^{226}Ra et les paramètres associés ont été calculés par une analyse statistique des résultats. En tout cas, les valeurs recommandées s'accordent en moins de deux pour cent des radioactivités prédites en assumant l'equilibre radioactif pour la suite de désintégration d'l'uranium-238.

Les valeurs recommandées de la radioactivité du radium sont 1,40; 15,5; 31,5; 857 Bq g^{-1} pour le DL-1a, BL-4a, DH-1a et BL-5, respectivement.

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*Research Scientists, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa/
*Chercheurs scientifiques, Laboratoires des sciences minérales, CANMET, Energie, Mines et Ressources Canada, Ottawa.

CONTENTS

	Page
SYNOPSIS	1
INTRODUCTION	1
INTERLABORATORY PROGRAM	1
DETERMINATION OF RECOMMENDED VALUES AND ESTIMATION OF UNCERTAINTIES	2
DISCUSSION OF RESULTS	5
REFERENCES	8
APPENDIX A - PARTICIPATING LABORATORIES	A-11
- REPORTS BY CONTRACTING LABORATORIES	A-12
APPENDIX B - SUMMARY OF METHODS	B-15
APPENDIX C - ESTIMATION OF HOMOGENEITY OF RADIUM IN BL-5	C-21
REFERENCES FOR APPENDICES	C-23

TABLES

1	Recommended values and statistical parameters for ^{226}Ra, Bq g^{-1}	2
2	Results, laboratory means, and standard deviations for ^{226}Ra in DL-1a	3
3	Results, laboratory means, and standard deviations for ^{226}Ra in BL-4a	3
4	Results, laboratory means, and standard deviations for ^{226}Ra in DH-1a	4
5	Results, laboratory means, and standard deviations for ^{226}Ra in BL-5	4
6	Comparison of recommended ^{226}Ra activities with those predicted for $^{238}U/^{226}Ra$ secular equilibrium	5
7	Values of σ_B/σ_A and RP for ^{226}Ra	7
8	Reports submitted by participants under contracts	A-12
9	Summary of radiochemistry methods	B-15
10	Summary of ^{226}Ra measurement methodology	B-16
11	Net photopeak count rates for 1-g samples of BL-5	C-22
12	Analysis of variance for gamma-ray spectrometry intensities	C-22
13	Estimation of components of variance	C-23

FIGURES

1	Distribution of within-laboratory mean activities for ^{226}Ra about consensus means	6

INTRODUCTION

There is a need for compositional reference materials for important members of the ^{238}U decay series, principally in the monitoring of hazardous isotopes that are byproducts of uranium-ore processing, and in the radiometric measurement of uranium, particularly in geological exploration. In the former application, isotopes of primary interest include ^{226}Ra, ^{210}Pb, ^{210}Po, and ^{230}Th. In the latter, uranium content is normally predicted from ^{214}Bi and/or ^{214}Pb gamma-ray measurements. The accuracy of this prediction depends on the $^{222}Rn/^{226}Ra/^{238}U$ activity ratios, i.e., the degree of secular equilibrium in the decay series.

The interlaboratory program to estimate the activity of ^{226}Ra in DL-1a, BL-4a, DH-1a and BL-5 described herein is the first phase of an endeavour by the Canadian Certified Reference Materials Project (CCRMP) to provide state-of-the-art radiochemical information about these uranium and uranium/thorium ore materials (1-4).

DL-1a and DH-1a are respectively waste rock and hand-picked ore grade material from Denison Mines, Elliot Lake, Ontario. The principal radioactive minerals are uraninite and brannerite. BL-4a is a composite of materials from the Fay and Verna mines, Beaverlodge operations, Eldorado, Saskatchewan. The sole radioactive mineral is pitchblende. BL-5 is a hand-picked sample from Beaverlodge corresponding to a low grade concentrate in uranium concentration. The radioactive mineral is uraninite. Preliminary radiochemical measurements indicated that the ^{238}U decay series was close to secular equilibrium in DL-1a, DH-1a, and BL-5.

INTERLABORATORY PROGRAM

Thirteen independent laboratories contributed results for ^{226}Ra activities in replicate samples of each ore. Five laboratories applied alpha spectrometry techniques following radiochemical separation of radium (αs), two others used gross alpha counting following radium isolation applying appropriate counting delay periods to minimize ^{238}Ra and ^{224}Ra interference effects ($g\alpha$). Three laboratories applied radon emanation techniques to dissolved samples (Rn) and three others applied gamma-ray spectrometry methods, either with or without sample pretreatment (γ). Participating laboratories and methodology summaries appear in Appendices A and B respectively.

Participants were provided with one or more bottles of each material selected at random from stock and were asked to provide independent determinations in quadruplicate on samples with a minimum mass of 1 g. Calibrations were to be performed with radium solutions from NBS: these have 99% confidence uncertainties of less than 2% in radium mass. The specific activity 3.657×10^{10} Bq g^{-1} ^{226}Ra was recommended for the activity conversion (5,6). Where feasible, counting periods were targeted to yield sufficient data such that net count uncertainties for each sample and standard measurement were less than 0.4% (1σ), with the exception of DL-1a where the target was 1%.

The factor 0.03700 Bq/pCi was used to convert results reported in pCi/g.

DETERMINATION OF RECOMMENDED VALUES AND ESTIMATION OF UNCERTAINTIES

The recommended (consensus) value for ^{226}Ra activity is defined as the grand mean of all individual determinations after physical and statistical outliers are excluded. Dixon's r_{21} statistic at the 5% critical level was applied to the within-laboratory mean values to identify probable outliers (7). There was, however, no evidence for either physical or statistical outliers, and all results were used to compute the consensus values.

A one-way analysis of variance was performed to estimate the uncertainty in the consensus value (8). The statistical model applied is described in the certification publications for these materials (1,3,4). The $F_{0.95}$ statistic for the appropriate degrees of freedom demonstrated that the between-laboratory component of variance was significantly greater than the within-laboratory component.

Recommended ^{226}Ra activities and related statistical parameters are presented in Table 1. The 95% confidence limits (CL) are the expected range within which the consensus value would be found in 95 out of 100 cases of repetition of the identical program. Analytical information is presented in Tables 2 to 5.

Table 1 - Recommended values and statistical parameters for ^{226}Ra, Bq g^{-1}

Material	No. of laboratories	No. of results	Mean	95% CL Low	95% CL High	s_A
DL-1a	13	54	1.40	1.36	1.44	0.05
BL-4a	13	52	15.5	15.0	16.0	0.4
DH-1a	13	55	31.5	30.4	32.6	0.8
BL-5	11	43	857	819	895	28

Table 2 - Results, laboratory means, and standard deviations for ^{226}Ra in DL-1a

		Bq g^{-1}					Mean	S.D.
Lab-1	(as)	1.299	1.306	1.288	1.294		1.297	0.007
Lab-2	(gs)	1.39	1.38	1.52	1.49		1.45	0.07
Lab-3	(γ)	1.432	1.451	1.444	1.444		1.443	0.008
Lab-4	(Rn)	1.413	1.499	1.453	1.362		1.415	0.056
		1.348	1.351	1.446	1.445			
Lab-5	(as)	1.425	1.527	1.553	1.422		1.482	0.068
Lab-6	(as)	1.409	1.470	1.516	1.455		1.463	0.044
Lab-7	(γ)	1.254	1.277	1.269	1.254		1.264	0.011
Lab-8	(Rn)	1.449	1.390	1.430			1.423	0.030
Lab-9	(gs)	1.52	1.56	1.25	1.41		1.43	0.14
Lab-10	(Rn)	1.437	1.265	1.375	1.393		1.368	0.073
Lab-11	(as)	1.374	1.321	1.344	1.341		1.345	0.022
Lab-12[a]	(as)	1.436	1.528				1.482	0.065
Lab-13	(γ)	1.405	1.497	1.388	1.402	1.354	1.409	0.053
				Grand mean 1.403				

[a]Measurement uncertainty ±0.019

Table 3 - Results, laboratory means, and standard deviations for ^{226}Ra in BL-4a

		Bq g^{-1}					Mean	S.D.
Lab-1	(as)	15.30	15.43	15.09	15.35		15.29	0.15
Lab-2	(gs)	15.9	17.0	16.3	15.1	14.8	15.8	0.9
Lab-3	(γ)	16.17	16.11	15.80	15.93		16.00	0.17
Lab-4	(Rn)	14.62	15.20	15.10	14.49		15.27	0.56
		15.22	15.93	15.56	16.03			
Lab-5	(as)	16.28	15.55	16.43	17.95		16.55	1.01
Lab-6	(as)	15.29	15.43	15.69	15.86		15.57	0.26
Lab-7	(γ)	13.39	13.54	13.43	13.43		13.45	0.06
Lab-8	(Rn)	17.00	16.57	16.99	16.27		16.71	0.35
Lab-9	(gs)	15.5	16.0	15.2	15.8		15.6	0.35
Lab-10	(Rn)	13.86	15.47	14.52	15.54		14.85	0.81
Lab-11	(as)	14.21	14.48	14.61	15.30		14.65	0.46
Lab-12[a]	(as)	15.73	15.54				15.64	0.13
Lab-13	(γ)	15.61	15.84	16.26	15.85	16.11	15.93	0.25
				Grand mean 15.48				

[a]Measurement uncertainty ±0.09

Table 4 - Results, laboratory means, and standard deviations for ^{226}Ra in DH-1a

		Bq g^{-1}						Mean	S.D.
Lab-1	(αs)	26.89	29.00	27.77	28.50			28.04	0.92
Lab-2	($g\alpha$)	32.9	31.8	31.3	32.4			32.1	0.7
Lab-3	(γ)	32.53	32.53	32.84	32.72			32.66	0.15
Lab-4	(Rn)	30.20	31.25	29.65	30.69			30.48	0.52
		30.32	30.13	30.54	31.04				
Lab-5	(αs)	34.90	32.02	35.77	34.66			34.34	1.62
Lab-6	(αs)	33.12	32.15	32.49	33.30			32.77	0.54
Lab-7	(γ)	29.19	27.94	28.60	28.31			28.51	0.53
Lab-8	(Rn)	31.78	31.61	32.74	31.70			31.96	0.53
Lab-9	($g\alpha$)	31.1	33.1	34.5	33.1			32.9	1.4
Lab-10	(Rn)	31.56	28.56	34.16	29.99			31.07	2.40
Lab-11	(αs)	30.83	31.26	31.14	31.43			31.17	0.25
Lab-12*	(αs)	31.41	31.08					31.25	0.23
Lab-13	(γ)	32.38	32.96	32.20	33.52	32.54		32.72	0.53
				Grand mean 31.49					

*Measurement uncertainty ±0.15

Table 5 - Results, laboratory means, and standard deviations for ^{226}Ra in BL-5

		Bq g^{-1}						Mean	S.D.
Lab-1	(αs)	770	768	802	802			785	19
Lab-2	($g\alpha$)	821	934	824	843	859	896	863	44
Lab-3	(γ)	905	898	894	906			901	6
Lab-4	(Rn)	870	867	857	854			859	13
		858	872	831	865				
Lab-5	(αs)	801	959	1007	1032			950	104
Lab-6	(αs)	815	834	841	832			830	11
Lab-7	(γ)	762	760	765	765			763	2.4
Lab-9	($g\alpha$)	857	951	849	810			867	60
Lab-10	(Rn)	776	829	767	812			796	29
Lab-11	(αs)	867	886	893	856			875	17
Lab-13	(γ)	929	910	912	906	947		921	17
				Grand mean 857					

DISCUSSION OF RESULTS

STATE OF SECULAR EQUILIBRIUM

In Table 6, the recommended ^{226}Ra activities are compared with those predicted assuming secular equilibrium, i.e., a $^{238}U/^{226}Ra$ activity ratio of 1.000. The specific activity 12.4365 ± 0.0068 kBq g^{-1} ^{238}U and 99.274% abundance for this isotope were used (9,10). Recommended uranium concentrations were used (1-4), and the uncertainty estimates were propagated from estimated component uncertainties. The results confirm that ^{226}Ra is close to, if not in, secular equilibrium in each material: there is no statistical significance in the difference between the recommended ^{226}Ra activities and those predicted assuming secular equilibrium.

Table 6 - Comparison of recommended ^{226}Ra activities with those predicted for $^{238}U/^{226}Ra$ secular equilibrium

Material	% U	^{226}Ra activity ratio (recommended/ equilibrium)	± 95% Confid.
DL-1a	0.0116	0.980	0.039
BL-4a	0.1248	1.004	0.035
DH-1a	0.260	0.981	0.036
BL-5	7.09	0.980	0.044

PRECISION OF MEASUREMENTS

Within-laboratory standard deviations for replicate measurements generally exceeded the values predicted from counting statistics alone. The observed variances consequently reflect methodology repeatability. It is likely that radium concentration variance between samples (inhomogeneity) is an insignificant component of the observed variances, e.g., Appendix C.

The results of this program revealed no consistent evidence for precision superiority by a particular method. Gamma-ray spectrometry measurements that require no chemical pretreatment should intrinsically be subject to lower methodology variance: however, comparable reproducibility is achievable by other methods in a number of instances (Fig. 1). Relationships between precision and either activity per gram or the nature of the ore (uranium or uranium-thorium) were also not evident from the results.

BETWEEN-LABORATORY BIAS

Although the effect is somewhat masked by within-laboratory variances, there is a general tendency for the magnitude of the mean values from the laboratories to retain a consistent order for all four reference materials. This, of course, indicates between-laboratory bias that can likely be attributed to calibration bias and/or systematic calibration/measurement differences.

TRACEABILITY

The 95% confidence intervals for the recommended values of ^{226}Ra activity indicate the current state of consensus achievable for compositional ore materials by experienced analysts using accepted techniques. Because 12 of the 13 participating laboratories used the certified radium standards of NBS (total mass uncertainties <2%) for calibration procedures, the recommended values for ^{226}Ra activity for DL-1a, BL-4a, DH-1a and BL-5 are traceable to these standards and the specific activity 3.657×10^{10} Bq g^{-1}.

QUALITY OF CERTIFICATION DATA

The ratio of the between-laboratory to the within-laboratory standard deviation, σ_B/σ_A, where

$$\sigma_B = \sum_{i}^{k} (\bar{x}_i. - \sum_{i}^{k} \bar{x}_i.)/k \quad ^2 \quad k - 1$$

is a measure of the quality of the certification data based on the results of the elemental analysis of the reference materials of CCRMP (11). The acceptable upper limit for σ_B/σ_A is 3.

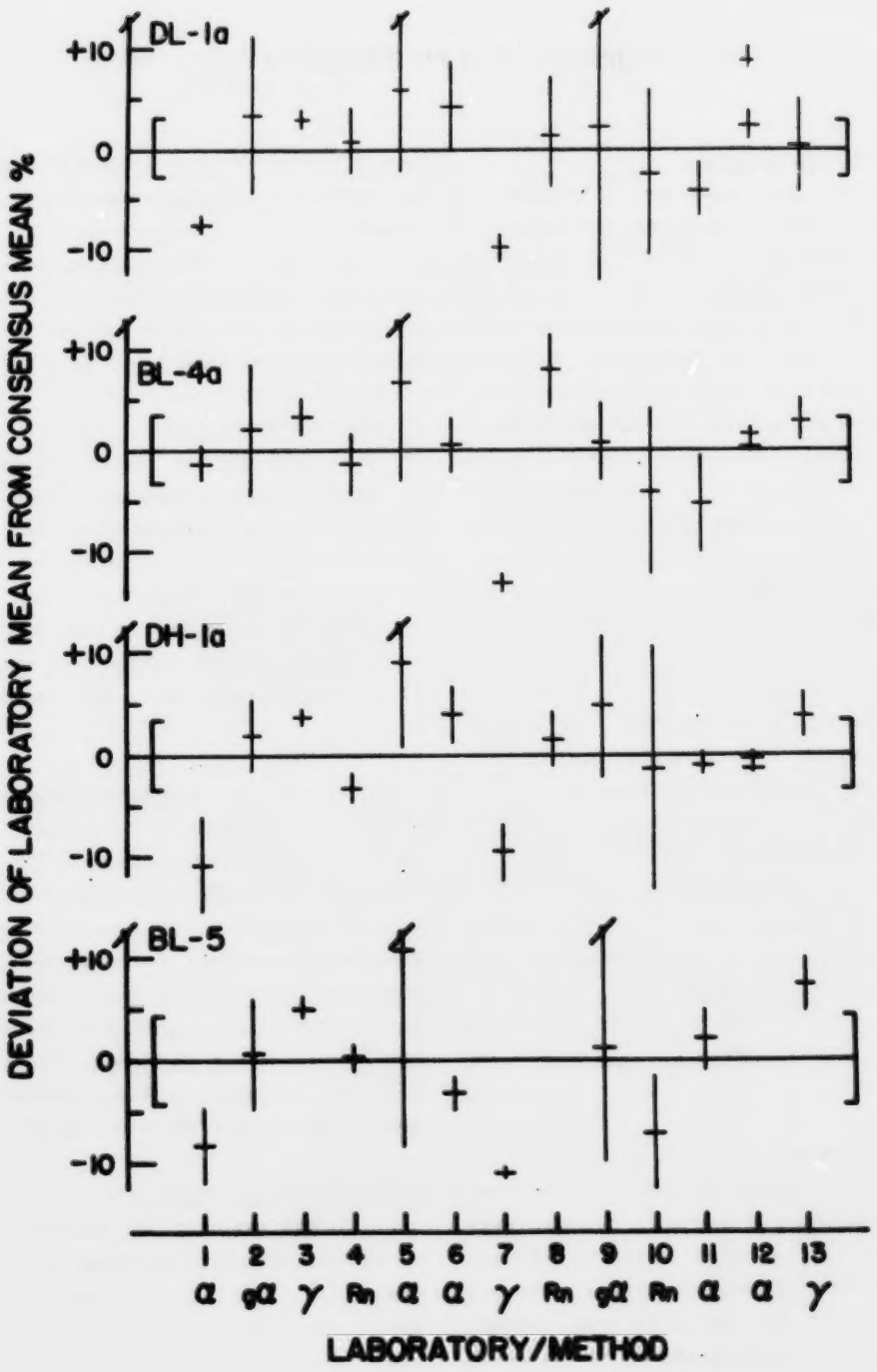

Fig. 1 - Distribution of within-laboratory mean activities for ^{226}Ra about recommended values. Vertical bars are 95% confidence interval estimates from replicate values. Brackets indicate the 95% confidence interval for the recommended values. Results from Laboratory 12 are shown individually with individual uncertainty estimates.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP should not exceed 15%.

There is no *a priori* reason to conclude that the certification data for a radionuclide are of acceptable quality only if they satisfy the criterion for certification derived for elemental analysis. Table 7, nevertheless, illustrates that the present interlaboratory data for ^{226}Ra do. The relatively high within-laboratory standard deviations of some laboratories, e.g., No. 9, 10, 5 and 5 for DL-1a, DH-1a, BL-4a and BL-5, respectively, increase the value of σ_A, thereby favouring a lower value for σ_B/σ_A. However, even when these laboratories are excluded from the calculation of σ_A, a value of $\sigma_B/\sigma_A < 3$ is obtained with RP = 0.0. These results suggest that serious consideration be given to the assessment of the quality of the data from future interlaboratory programs for ^{226}Ra (and possibly other radionuclides) by the same criterion applied to elemental analysis data.

Table 7 - Values of σ_B/σ_A and RP for ^{226}Ra

RM	Number of sets of results	σ_B/σ_A All results	RP %
DL-1a	13	1.30	0.0
BL-4a	13	2.02	0.0
DH-1a	13	2.23	0.0
BL-5	11	1.98	0.0

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APPENDIX A

PARTICIPATING LABORATORIES
REPORTS BY CONTRACTING LABORATORIES

PARTICIPATING LABORATORIES

Lab-1: University of Calgary, Department of Physics, Calgary, Alberta.
C.J. Bland and P. Jarvis

Lab-2: Saskatchewan Research Council, Analytical Chemistry Division, Saskatoon, Saskatchewan.
G. Smithson, V. Penner, and R. Ortlepp

Lab-3: a) Geological Survey of Canada, Ottawa, Radiation Geophysics Section.
R.L. Grasty

Lab-4: b) Geological Survey of Canada, Ottawa, Geochemistry Exploration Research Section.
W. Dyck, J.C. Pelchat, and H. Schneeberger

Lab-5: B.C. Research, Division of Extractive Metallurgy, Vancouver, British Columbia.
B. Caughlin, G.P. Lee and R.W. Lawrence

Lab-6 : Monenco Analytical Laboratories, Calgary, Alberta.
N. Chiu and J. Dean

Lab-7: Los Alamos National Laboratory, Group H-8, Environmental Surveillance, Los Alamos, New Mexico.
E.S. Gladney

Lab-8: Fisheries and Oceans Canada, Freshwater Institute, Winnipeg, Manitoba.
P. Wilkinson, N. Vasudeva, and D. Fox

Lab-9: Atomic Energy Control Board, Directorate of Fuel Cycle and Materials Regulation, Ottawa, Ontario.
R.A. Washington, E.C. Laishley, and D.F. Sullivan

Lab-10: Denison Mines Ltd., Elliot Lake, Ontario.
Doo-Hong Kim

Lab-11: University of Waterloo, Waterloo Research Institute, Waterloo, Ontario.
H.D. Sharma and B. Hauk

Lab-12: E.G. & G. Idaho, Inc., P.O. Box 1625, Idaho Falls, Idaho, 83415.
C.W. Sill

Lab-13: Canada Centre for Mineral and Energy Technology, Mineral Sciences Laboratories, Chemical Laboratory, Ottawa, Canada.
C.W. Smith, J.L. Dalton and R.H. McCorkell

Table 8 - Reports submitted by participants under contracts completed January, 1983*

Laboratory	Title	Contract**	
		Requisition No.	Serial No.
Physics Department, University of Calgary	Determination of radium-226 in uranium-bearing reference materials for certification purposes	23440-2-9064-1	OSQ82 00085
Waterloo Research Institute, University of Waterloo	Determination of radium-226 in uranium-bearing reference materials for certification purposes	23440-2-9064-2	OSQ82 00086
Analytical Chemistry Division, Saskatchewan Research Council	Determination of radium-226 in uranium-bearing reference materials for certification purposes	23440-2-9064-3	OSQ82 00087
Extractive Metallurgy Division, B.C. Research	Determination of radium-226 in uranium-bearing reference materials for certification purposes	23440-2-9064-4	OSQ82 00088
Monenco Analytical Laboratories, Calgary, Alberta	Determination of radium-226 in uranium-bearing reference materials for certification purposes	23440-2-9064-5	OSQ82 00089

*Reports filed with Research Program Office, Canada Centre for Mineral and Energy Technology, 555 Booth St., Ottawa, Ontario, Canada K1A 0G1.

**Funded under CANMET Minerals and Earth Sciences Program, Reference Materials Project (380001).

APPENDIX B

SUMMARY OF METHODS

Table 9 - Summary of radiochemistry methods

	Subsample (Range, g)	Decomposition	Radium separation[a]	References
Lab-1 (αs)	1-4	HNO_3,HF,KF fusion, pyrosulphate fusion	$Pb(Ba)SO_4$/EDTA/$BaSO_4$*	1,2
Lab-2 (αs)	1	HF,H_2SO_4, pyrosulphate fusion	$Pb(Ba)SO_4$/EDTA/$BaSO_4$*	3
Lab-3 (γ)	3-300	(blended with silica powder to approx. 2 kBq/300 g; sealed in can)		4,5
Lab-4 (Rn)	1	HNO_3HF,HCl	(radon emanation from 3.3% HCl soln.)	
Lab-5 (αs)	1	HNO_3,$HClO_4$,HF	$BaSO_4$/DTPA/$BaSO_4$*	6
Lab-6 (αs)	1	KF fusion, pyrosulphate fusion	$Pb(Ba)SO_4$/DTPA/$BaSO_4$*	3,7,8,9
Lab-7 (γ)	20-80	(standard geometry metal cans filled with ore, sealed)		10
Lab-8 (Rn)	0.5	HF,HNO_3,$HClO_4$,H_2SO_4, pyrosulphate fusion	(radon emanation from 0.15 N EDTA)	11
Lab-9 (αs)	1	Na_2CO_3 fusion	$Pb(Ba)SO_4$/EDTA/$BaSO_4$**	12
Lab-10 (Rn)	0.5	H_2SO_4,HF, $NaClO_3$/$Na_2B_4O_7$(3:1)/80 mg $BaSO_4$ fusion	ignite $BaSO_4$/ash,HF,H_3PO_4,HCl; radon eman. from 20% HCl soln.	
Lab-11 (αs)	1-2	HF,H_2SO_4, pyrosulphate fusion	$Pb(Ba)SO_4$/DTPA/$BaSO_4$*	
Lab-12 (αs)	0.25-0.5	HNO_3,KF fusion, pyrosulphate fusion	$Pb(Ba)SO_4$/DTPA/$BaSO_4$*	13
Lab-13 (γ)	0.5-10	(HNO_3,HF,HSO_4; residue ignited, fused with $Li_2B_4O_7$, cast as glass discs; no acid digestion for BL-4a or BL-5)		

a - $Pb(Ba)SO_4$/EDTA/$BaSO_4$ refers to separation of radium from the matrix solution by coprecipitation with lead and barium carriers as sulphates, followed by dissolution in the presence of ethylenediaminetetraacetate and selective precipitation of $Ba(Ra)SO_4$. DTPA refers to diethylenetriaminepenta acetate.

* Indicates that barium (radium) recovery fraction measured by gamma spectrometry measurement of ^{133}Ba added as a tracer.

** Barium (radium) recovery fraction measured by atomic absorption spectrophotometric measurement of barium following radiochemical measurements.

Table 10 - Summary of ^{226}Ra measurement methodology

	Method/logy[a]	^{226}Ra calibration SRM[aa]	References
Lab-1	(αs) SBD, 4.78 + 4.59 MeV ^{226}Ra, correction for higher energy tailing interference. Filtration sleeve is base of counting chamber.	NBS 4957 (1.8%)	2
Lab-2	(g_α) ZnS-mylar/PMT. ^{222}Rn + daughter ingrown for specific period. Correction for ^{223}Ra.	NBS 4953-C (1.3%)	3
Lab-3	(γ) NaI(Tl), two 5 x 5's. ^{214}Bi 1660-1860 keV, corrected for spectral interferences from ^{40}K and ^{208}Tl. Sealed >30 d.	NBS 4957 (1.8%)	4,5
Lab-4	(Rn) Lucas cell/PMT, corrected for $^{222}Rn/^{226}Ra$ equilibrium state. Transfer via air flush from 295 mL of soln. sealed for known time.	NBS 4955 (3.6%) NBS 4957 (1.8%)	14
Lab-5	(αs) SBD	NBS 4957 (1.8%)	
Lab-6	(αs) SBD. ^{226}Ra α photopeak counted prior to tailing ingrowth interference.	NBS 4957 (1.8%)	
Lab-7	(γ) Ge(Li), ^{214}Bi 609 KeV, sealed >30 d.	NBS 4958 (1.8%)	10
Lab-8	(Rn) Lucas cell/PMT. Rn trapped on activated C (-50°C) with He flush. Released at 450°C via He flush to evacuated cell.	NBS 4953-C (1.3%)	15,16
Lab-9	(g_α) FPC/cosmic guard detector. Decay interval to minimize ^{224}Ra, ^{223}Ra interference, and permit theoretical ingrowth of ^{226}Ra daughters.	NBS 4964-B (0.5%)	
Lab-10	(Rn) Lucas cell/PMT. Air flush from flushing tube into evacuated flask after known ingrowth period.	EPA 1907-1-14 (10.2%)	17
Lab-11	(αs) SBD. ^{226}Ra α photopeak counted prior to significant ingrowth interference from tails of higher energy photopeaks.	NBS 4959 (1.3%)	
Lab-12	(αs) SBD. ^{226}Ra α photopeak. Optimized Ba(Ra)SO_4 isolation procedures permitted 75-85 KeV FWHM resolution with no tailing interferences.		13
13	(γ) HPGe 56 cm^3 true coaxial, ^{214}Pb + ^{214}Bi (295 + 352 + 609 KeV) after >30 d.	NBS 4959 (1.3%)	

[a]abbreviations: (αs) SBD - alpha particle spectrometry using a silicon surface-barrier detector; (g_α) - gross (total) alpha particle counting; (γ) - gamma-ray spectrometry; (Rn) - radon counting; PMT - photo mulitplier tube; FPC - flow-proportional counter; HPGe - high-purity germanium; FWHM - full width at half-maximum.

[aa]NBS = U.S. National Bureau of Standards. Values in brackets are published uncertainties in stated μg radium at 99% confidence.

EPA = U.S. Environmental Protection Agency reference solution.

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APPENDIX C

ESTIMATION OF HOMOGENEITY OF RADIUM IN BL-5

ESTIMATION OF HOMOGENEITY OF RADIUM IN BL-5

The degree of homogeneity of ^{226}Ra in BL-5 was estimated by statistical analysis of associated gamma-ray photopeak intensities from 1-g subsamples taken from 10 bottles selected at random.

Weighed 1-g samples were transferred to 3.18-cm diam aluminum caps and pressed into uniform discs at 140 MPa in a pellet press. The open face was sealed with mylar film and the disc was then mounted on the end window of a 56-cm^3 coaxial germanium spectrometer. The spectrum was acquired for 4500 s.

Radium-226 exhibits only one gamma-ray photopeak at 186.2 KeV of sufficient intensity to be useful; however, this is unresolved from a photopeak at 185.7 KeV due to ^{235}U (1). Measurements under the present experimental conditions indicate relative contributions of about 58:42 (^{226}Ra:^{235}U) to the unresolved photopeak for an ore at secular equilibrium. This photopeak is consequently useful only to estimate the combined homogeneity (radium plus uranium), however, uranium homogeneity has been demonstrated (2).

An indirect estimation of ^{226}Ra homogeneity independent of uranium can be obtained from statistical analysis of photopeaks due to ^{214}Pb and ^{214}Bi, since the activities of these isotopes are proportional to the ^{226}Ra activity. This presupposes that the ^{222}Rn emanation rate is minor since gas diffusion could then possibly redistribute these radon daughter activities. The emanation rate of BL-5 has been measured as 2.9 $\pm$ 0.6% (3). The photopeaks at 242.0, 295.4 and 352.0 KeV (^{214}Pb) and 609.3 KeV (^{214}Bi) were used for the homogeneity estimate. The summed intensity of these photopeaks (I) was used in order to reduce the counting statistics contribution to the variance. Measurement data are shown in Table 11.

Results of the analysis of variance (Table 12) demonstrate that there is no significant difference between the within- and between-bottle variance (4).

The observed variance in the sample response for a given photopeak contains components arising from variances in the radium activity, sample preparation, spectrometer response and counting statistics. The last two contributions were estimated independently, the former by counting a monitor interspersed with the sample measurements, and the latter from integral and background counts and the estimate $\sigma N \approx \sqrt{N}$ (5).

The estimations of components of variance are shown in Table 13. The residual component, calculated as (observed^2-counting statistics^2-response^2)$^{1/2}$, estimates the combined relative standard deviation attributable to sample preparation (mass geometry) and any radium inhomogeneity contributions. The distribution of ^{226}Ra in 1-g samples of BL-5 is consequently estimated as having a coefficient of variation of considerably less than 1%.

Table 11 - Net photopeak count rates for 1-g samples of BL-5

Bottle (sample)	Photopeak count rate, $s^{-1} g^{-1}$				
	186 KeV	352 KeV	609 KeV	$I(^{214}Bi + ^{214}Pb)$	$I/(^{226}Ra + ^{235}U)$
1 (a)	8.30	21.63	11.49	53.7	6.47
(b)	8.52	22.03	11.83	54.9	6.44
(c)	8.47	22.16	11.74	55.3	6.53
(d)	8.45	22.24	11.98	55.5	6.56
(e)	8.36	22.02	11.71	54.6	6.53
(f)	8.50	22.18	11.83	55.2	6.50
2 (a)	8.39	22.07	11.69	54.7	6.52
(b)	8.49	22.08	11.72	54.8	6.46
(c)	8.44	22.10	11.71	55.0	6.52
(d)	8.44	22.32	11.82	55.4	6.57
(e)	8.27	21.88	11.59	54.4	6.58
(f)	8.45	22.14	11.71	54.9	6.50
3	8.35	21.79	11.66	54.1	6.47
4	8.27	21.73	11.65	54.3	6.57
5	8.37	22.35	11.89	55.3	6.61
6	8.33	22.00	11.72	54.6	6.56
7	8.47	22.27	11.78	55.2	6.51
8	8.48	22.20	11.71	55.3	6.52
9	8.62	22.33	11.91	55.7	6.46
10	8.49	22.22	11.74	55.4	6.52
Mean:	8.41	22.09	11.73	54.8	6.52
Std. dev.:	0.11	0.20	0.12	0.52	0.046

Table 12 - Analysis of variance for gamma-ray spectrometry intensities

Source	Degrees of freedom	Mean square		
		186 KeV	609 KeV	$I(^{214}Bi + ^{214}Pb)$
Between bottles	9	1.0572×10^{-2}	9.4923×10^{-3}	2.5693×10^{-1}
Within bottles	10	6.7346×10^{-3}	1.6087×10^{-2}	2.7589×10^{-1}
F ratio		1.570	0.5901	0.9313

$F_{0.05}(9,10) = 3.02$; the null hypothesis of no difference between within- and between-bottle variance is accepted (4).

Table 13 - Estimation of components of variance

Source	Relative standard deviation, %				
	186 KeV	352 KeV	609 KeV	$\Sigma(^{214}Bi + ^{214}Pb)$	$\Sigma/(^{226}Ra + ^{235}U)$
Observed	1.31	0.91	1.02	0.95	0.71
Counting statistics	0.92	0.42	0.56	0.27	0.92
Spectrometer response	0.9	0.5	0.5	0.6	-
residual	0.3	0.6	0.7	0.7	-

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